PATENT ABSTRACTS OF JAPAN

(11)Publication number : 04-231545
(43)Date of publication of application : 20.08.1992

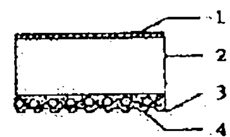
(51)Int.Cl. E04F 13/14
B32B 9/00

(21)Application number : 02-416324
(22)Date of filing : 28.12.1990

(71)Applicant : TOYOBO CO LTD
(72)Inventor : OCHI SEIICHI
AKEYAMA ISAMU

(54) POLLUTION-RESISTANT NATURAL ROCK MATERIAL

(57)Abstract:
PURPOSE: To obtain a pollution resistant natural rock material excellent in bending strength of an natural rock material, impact resistance, adherence to grounds such as mortar, and provided with excellent characteristics against various kinds of stains from the front and rear of the rock material before and after execution.
CONSTITUTION: The rear of an ultrathin rock material 2 is lined and reinforced with coarsely-woven cloth 3 and corrosion-resistant resin 4, the reinforced is uneven and, at the same time, fluorine corrosion resistant layer 1 is formed on the front of the rock material. According to the constitution, bearing strength of the ultrathin natural rock material, impact resistance, adherence and pollution resistance are excellent.



LEGAL STATUS
[Date of request for examination]
[Date of sending the examiner's decision of rejection]
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
[Date of final disposal for application]
[Patent number]
[Date of registration]
[Number of appeal against examiner's decision of rejection]
[Date of requesting appeal against examiner's decision of rejection]
[Date of extinction of right]

DERWENT-ACC-NO: 1992-326933
DERWENT-WEEK: 199240

TITLE: Stainless natural stone material for walls, floors, etc. - in which back of thin stone plate is reinforced by coarse woven cloth and corrosion-resistant resin

PATENT-ASSIGNEE: TOYOBO KK [TOYM]

PRIORITY-DATA:
1990JP-0416324 (December 28, 1990)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 04231545 A	August 20, 1992	N/A	007	E04F 013/14

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP04231545A	N/A	1990JP-0416324	December 28, 1990

INT-CL (IPC): B32B009/00; E04F013/14
ABSTRACTED-PUB-NO: JP04231545A

BASIC-ABSTRACT:
In a stainless natural stone material, the back side of a thin stone plate is reinforced by a coarse woven fabric and a corrosion-resistant resin in an uneven form, and a stainless (or staining resistant) fluororesin layer is formed on the surface of the thin stone material.

The back side of a thin natural stone plate of 2-12 mm is reinforced by a coarse woven fabric of glass fibre, polyester fibre, etc. which is treated with an alkali-resistant, resin such as methylolmelamine resin,

acryl resin, etc.,
and the surface of the stone material is covered with a fluororesin layer of
PTFE etc.

USE/ADVANTAGE - The stainless natural stone material to be used as wall, floor
etc. construction work etc. has excellent bending strength, impact resistance,
adhesion and staining resistance

CHOSEN-DRAWING: Dwg.0/8

DERWENT-CLASS: A93 L02 P73 Q45

CPI-CODES: A04-E10; A12-B07; A12-R01; A12-S08; L02-D07;

(19)日本国特許庁（ＪＰ）　(12) 公開特許公報（Ａ）　(11)特許出願公開番号
特開平4－231545
(43)公開日　平成４年(1992) ８月20日

(51)Int.Cl.⁵	識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ｅ０４Ｆ　13/14	１０１	7023－2Ｅ		
Ｂ３２Ｂ　9/00	Ｚ	7365－4Ｆ		

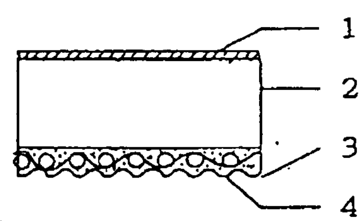
審査請求　未請求　請求項の数１（全　７　頁）

(21)出願番号　特願平2－416324
(22)出願日　平成２年(1990) 12月28日

(71)出願人　000003160
東洋紡績株式会社
大阪府大阪市北区堂島浜２丁目２番８号
(72)発明者　越智　清一
滋賀県大津市堅田二丁目１番１号　東洋紡績株式会社総合研究所内
(72)発明者　明山　勇
大阪市北区堂島浜二丁目２番８号　東洋紡績株式会社本店内

(54)【発明の名称】　防汚性天然石材

(57)【要約】　（修正有）
【目的】　本発明は、極薄天然石材の曲げ強度、耐衝撃性およびモルタル等下地との接着性にすぐれ、しかも施工前後の石材表裏面からの各種汚染に対して、優れた性質を示す防汚性天然石材を提供するにある。
【構成】　極薄石材２裏面に粗目織物３と耐食性樹脂４で、裏打ち補強し、補強面表面凹凸性を付与すると共に、石材表面フッ素系防汚剤層１を形成させる。
【効果】　極薄天然石材の曲げ強度、耐衝撃性、接着性および防汚性に優れる。



1　2

【特許請求の範囲】

【請求項1】　極薄天然石材の表面にフッ素系防汚剤、裏面に粗目補強布帛および耐食性樹脂層を有することを特徴とする防汚性天然石材。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は極薄天然石材に関する。さらに詳しくは、軽量、かつ強靱で施行性にすぐれ、しかも施工後、天然石材表面の光沢、色相および質感が低下しない防汚性天然石材に関する。

【0002】

【従来の技術】従来から、ダイヤモンドカッターを利用した薄切り技術による極薄天然石材は知られているが、この天然石材は軽量化の点ではすぐれた性質を示す反面、極薄のため、曲げ強度や耐衝撃性が低く、搬送性や施工性の問題に加え、施工後の、天然石材表裏面からの各種汚水や油分の浸透による汚れや、ほこり付着、さらに雨水、光による長期耐候性等に問題がある。

【0003】かかる欠点を改善するため、曲げ強度や耐衝撃性を向上させる方法としては、天然石材の裏面に繊維製布帛／樹脂で補強する方法（特公昭51－38731号公報、特公昭51－48972号公報）が提案されいる。しかし、このような方法では、石材裏面からの汚水浸透は改善できるものの、石材表面からの各種汚れ、例えば汚水や油分の浸透付着による汚れや、雨水、天然光、人工光による長期耐候性を大きく改良することはできず、極薄天然石材の長期安定使用には不十分である。

【0004】

【発明が解決しようとする課題】本発明は、極薄天然石材の軽量性の特徴を生かし、しかも、その欠点のひとつである曲げ強度と耐衝撃性を大幅に改善すると同時に、極薄のために特に発生し易い石材表裏面からの、各種汚水や油分の浸透による汚れや、ほこり付着、更には、雨水、光等の長期間の暴露による石材表面の光沢、色相および質感の経時変化を効果的に防止するものである。特に、天然石材の中で比較的軟質で多孔質の大理石や白御影石等の花崗岩は、極薄化するほど石材の強さが低下、汚水等の浸透による汚れが目立ちやすい傾向にある。これらの極薄天然石材の欠点をすべて解決することにより、軽量化による施工作業性の改善、従来法では実現しにくい大判天然石材による設計／施工の実現や、すぐれた防汚性を付与することで、天然石材本来の質感や高級感を効果的、かつ、永続的に保持させるものである。

【0005】

【課題を解決するための手段】極薄天然石材、特に比較的軟質、かつ多孔質の大理石や白御影石等の花崗岩について、これらの欠点である曲げ強度、耐衝撃性および外観品位の低下を同時に解決する方法を、鋭意研究の結果、本発明に到達した。すなわち、本発明は、極薄天然石材の表面にフッ素系防汚剤、裏面に粗目補強布帛および耐食性樹脂層を有することを特徴とする防汚性天然石材である。

【0006】更に詳しくは、厚さ2～12mm相当の極薄天然石材の表面に、耐候（光）性、耐熱性にすぐれ、しかも撥水性／撥油性に基づく防汚性を有する特殊フッ素系防汚剤を均一に付与する一方、石材裏面を、粗目補強布帛および耐食性樹脂にて裏打ち補強することで、極薄天然石材の欠点である曲げ強度、耐衝撃性を大幅に改善すると同時に、施工後、石材表面の外観品位の経時変化を防止できる防汚性天然石材を提供するものである。

【0007】本発明の極薄天然石材とは、2～12mm厚に薄切りされた天然石材である。適用原石は、大理石や、白御影石、赤御影石、黒御影石他の花崗岩等の広範囲の天然石が挙げられるが、特に、大理石や白御影石等の、比較的軟質かつ多孔質で、しかも汚れの目立ち易い色調の石材に対して効果的である。逆に、硬質かつ緻密で色調の濃い石材に対しては、長期使用時における光沢、質感の経時変化は防止できるが、各種汚水等による変化は、もともと本質的に少ない。

【0008】本発明のフッ素系防汚剤とは、ポリテトラフルオロエチレン、パーフルオロアルキル基含有アクリル系撥水撥油剤、パーフルオロアルキル基含有ウレタン系撥水撥油剤、およびこれらの変性物、例えば、シリコン変性フッ素系化合物やアルキレンオキサイド変性フッ素系化合物等が挙げられるが、耐候（光）性、耐熱性にすぐれ、しかも撥水性／撥油性に基づく防汚性を示すものであれば、特に、これらに限定されるものではない。かかる特徴を有する防汚剤としては、ポリテトラフルオロエチレンの乳化分散物、高フッ素含有型（固形分中のフッ素含量が、35％以上）アクリル系撥水撥油剤や、シリコン変性フッ素系撥水撥油剤が特に好ましい。

【0009】粗目補強布帛とは、ガラス繊維、カーボン繊維、ポリエステル系繊維、高強力高弾性ポリエチレン系繊維、および芳香族ポリアミド系繊維のいずれかで構成される編織物や不織布が挙げられるが、目的の一つである極薄天然石材の補強効果や耐食性樹脂による石材と補強布帛との複合化のし易さの点から、特に粗目織物が好ましい。かかる織物は一般的に、高強力、低伸度のものほど好ましく、その実現のために、ガラス繊維やカーボン繊維等と、ポリエステル系繊維や高強力高弾性ポリエチレン系繊維等との複合使用も効果的である。更に、これら粗目補強布帛は、セメントアルカリからの保護や作業性改善のため、予め、耐アルカリ性樹脂、例えばメチロールメラミン系樹脂、アクリル系樹脂、不飽和ポリエステル系樹脂、エポキシ系樹脂やエチレン酢酸ビニル系樹脂等で、硬仕上げ加工した後使用することもできる。

【0010】本発明における耐食性樹脂とは、各種薬品、例えば、酸、アルカリ、酸化剤、還元剤、各種塩類や有機溶剤等に対して、耐薬品性の優れた樹脂である。

【0011】かかる耐食性樹脂としては、通常、飽和ポリエステル系樹脂、不飽和ポリエステル系樹脂、例えば、ヘット酸ポリエステル、ビスフェノールAポリエステルや直鎖状ビニルポリエステル樹脂、あるいは、エポキシ系樹脂、例えば、グリシジルエーテル系、グリシジルエステル系、グリシジルアミン系、線状脂肪族エポキサイド系、脂環族エポキサイド系樹脂等が使用されるが、石材、補強布帛およびモルタル等の下地との接着性、補強効果、耐薬品性や防水性の点から、エポキシアクリレート系樹脂、ビスフェノールAポリエステル系樹脂が好ましい。

【0012】特に、耐食性の優れるエポキシアクリレート系樹脂を使用して、極薄天然石材裏面に良好な補強／防水効果を与えるためには、かかる樹脂にビニル系モノマー例えば、スチレンモノマー等を加え、20℃下、500センチポイズ以下、好ましくは100～300センチポイズに粘度調整後、硬化剤や硬化促進剤を必要量添加し、石材裏面表層部および補強布帛の繊維間隙に、均一かつ十分に浸透させた後、20～140℃下で、数分ないし1週間程度で硬化させる。

【0013】硬化剤や硬化促進剤は、メチルエチルケトンパーオキサイド（MEKPO）、ベンゾイルパーオキサイド（BPO）、ナフテン酸コバルト、オクテン酸コバルトやジメチルアニリンが挙げられる。通常、MEKPO／ナフテン酸コバルト系、BPO／ジメチルアニリン系が使用されるが、特に、室温硬化させたい場合は、MEKPO／ナフテン酸コバルト／ジメチルアニリン系の使用が有効である。

【0014】次ぎに、本発明における、フッ素系防汚剤、耐食性樹脂の付与方法について説明する。まず、フッ素系防汚剤は、極薄天然石材の表面部のみに適用される。具体的には、天然石材を所望の厚さに薄切り加工、表面研磨加工、乾燥後、まず石材裏面を粗目補強布帛および耐食性樹脂にて裏打ち補強した後、石材表面部にフッ系防汚剤を付与し、撥水撥油性に基づく防汚層を形成させる。

【0015】かかる防汚剤の、具体的付与方法としては、所定フッ素系防汚剤を水、又は水／有機溶剤液で0．1～20重量％、好ましくは2～10重量％に希釈した後、20～300ｇ／m2 相当量、好ましくは50～200ｇ／m2 相当量を、石材表面に均一に塗布、乾燥後、室温以上、140℃以下、好ましくは40～100℃下で数分ないし数時間硬化、被膜化する。かかる防汚剤は、石材表面の極表層部に、浸透斑なく、しかも、均一に付与することが、表面品位確保の点で望ましい。

【0016】一般的に、均質性に乏しい天然石材は、その種類、厚さおよび乾燥程度により防汚剤液の浸透度が微妙に異なるため、石材表面の極表層部に、防汚剤を均一に付与することは難しい。かかる問題点を解決するためには、防汚剤の種類、濃度付与量に加えて、石材の乾燥程度と防汚剤液の粘度管理が、極めて重要である。石材の乾燥程度の管理は、石材裏面の補強時の耐食性樹脂の硬化条件により異なるが、普通、硬化終了後、室温下で24時間以上養生した後、防汚加工される。又、防汚剤液の粘度管理は、使用防汚剤の種類、濃度により多少異なるが、石材表面からの過度の浸透や浸透斑を防止するため、100～3000センチポイズ、好ましくは200～1000センチポイズの範囲での使用が望ましい。防汚剤液の粘度が、100センチポイズ以下であれば、浸透斑が生じ、逆に3000センチポイズ以上では、防汚剤の表面付着斑が生じ易い。

【0017】引き続き、本発明における、石材裏面への耐食性樹脂の付与方法について説明する。かかる付与方法としては、①極薄天然石材裏面に粗目補強布帛を積層後、耐食性樹脂を塗布もしくは、注入する方法。②極薄天然石材裏面に耐食性樹脂を塗布後、粗目補強布帛を積層後、更に耐食性樹脂を塗布もしくは注入する方法。③予め耐食性樹脂を粗目補強布帛に含浸、硬化させ、シート状プリプレグとした後、極薄天然石材裏面に耐食性樹脂を塗布し、プリプレグを積層、接着させる方法等がある。耐食性樹脂の付与量は、適用天然石材の種類、厚さ、補強布帛の種類や石材の用途により異なるが、普通、100～1500ｇ／m^2 、好ましくは200～500ｇ／m^2 の範囲で選択して使用する。耐食性樹脂の硬化条件は、20～140℃、特に20～60℃が、裏打ち補強石材の反り変形防止や、石材物性および表面品位、例えば、光沢、色相等の保持の点から好ましい。尚裏打ち補強される天然石材の裏面は、適度の粗面性を有し、十分乾燥したものほど、良好な接着性を示す。

【0019】本発明において、裏打ち補強面とモルタルセメントや乾式接着剤との接着性を向上させる方法の一つとして、耐食性樹脂による裏打ち補強面の凹凸性形成方法がある。かかる方法としては、①粗目補強布帛の高低差を利用して耐食性樹脂の付与量をコントロールする方法。②耐食性樹脂表面にモルタル等の下地と接着性の良好な無機系粒子、例えばケイ砂等を100～1500ｇ／m^2 相当量を付与後、硬化させる方法。③耐食性樹脂表面に離形成凹凸状シートもしくはプレートを圧着、硬化後に剥離して付形する方法等が適用できる。

【0020】本発明における天然石材の表面とは、普通摩面側を、裏面とは、粗面側のことを意味する。

【0021】

【実施例】以下実施例をあげて、本発明を具体的に説明する。実施例において、％は全て重量％を示す。

【0023】防汚性天然石材の特性は、下記方法によって測定した。

【0024】1．　曲げ強度（曲げ破壊荷重）

各石材を幅5ｃｍ×長さ20ｃｍの大きさにカットした後、ＪＩＳ　Ａ　1408で定める方法で測定した（試料大きさ：5ｃｍ×20ｃｍ、曲げ速度：1mm／分、

曲げバーの曲率半径：５mm、支点間距離：１５cm）。

【００２４】２．　耐衝撃性

ＪＩＳ　Ａ　１４２１で定める方法に準拠し（試料大きさ：２０cm×２０cm、試料支持：砂上全面支持、おもり：W1 －１０００g、落下高さ：１００cm）、衝撃試験後の石材表面に変化無いものを○、ひびか入ったものを△、石材が破壊したものを×とした。

【００２５】３．　接着剤

縦横１０cm角の石材裏面に、厚さ５０mm相当量の調合モルタル（アドキープ：徳山曹達社製）を接着し、室温で３週間養生させた後、建研式引張試験器を用い接着力を測定した。

【００２６】４．　防汚性

＊縦横１０cm角の石材表裏面に、青インク２cc／リットル(l)、B重油５cc／lおよび粘土質１００g／lを含む、汚染水１０cc相当量を滴下、フィルムで被覆後、室温下、１週間放置後、濡れタオルで拭きとり、乾燥後の石材表裏面の汚染程度を、汚れが全く無いものを○、汚れが有るものを△、汚れが目立つものを×とした。

【００２７】５．　撥水性

縦横１０cm角の石材表面に、イソプロピルアルコール／水混合後の小滴を滴下して、濡れの状態を、１級（不良）～５級（良好）判定した。

【００２８】

【表１】

イソプロピルアルコール／水混合液組成物表

撥水性等級	組成（VOL%）	
	イソプロピルアルコール（試薬特級）	水
5	60	40
4	32	68
3	21	79
2	15	85
1	9	91

【００２９】６．　撥油性

ＡＡＴＣＣ－１１８－１９７５撥油性評価に準じて、石材表面の撥油性を測定し、１級（不良）～８級（良好）判定した。

【００３０】７．　フィールド防汚性

縦横５０cm角の石材裏面を、モルタルセメント下地に対して、水平に接着後、屋外で、２年間暴露試験後、石材表面の外観品位（光沢、色相）の変化を、変化が全く無いものを◎、変化が微妙なものを○、変化が小さいものを△、変化があるものを×と、目視判定した。

【００３１】８．　施工性

幅１m×長さ１．５m石材を用い、モルタル接着施工する場合の、横持ち作業性、接着作業性の難易度を総合的に示すもので、通常の厚さ１２mm以上の石材に比べて、容易であれば○、困難であれば×とした。

【００３２】実施例１

厚さ６mmの大理石の裏面に、ポリエステル長繊維（１０００d－１９２f、原糸強度８g／デニール）よりなる粗目織物（織密度縦横とも２０本／インチ）を重ね合わせ、エポキシアクリレート系耐食性樹脂（ネオポール８２５０L：日本ユピカ社製）１００部、８％ナフテン酸コバルト０．１部、５５％メチルエチルケトンパーオキサイド（パーメックＮ：日本油脂社製）１．０部からなる混合液４５０g／m² 相当量を塗布後、２５℃下５日間、硬化させ裏面表面に、微細な凹凸を有する補強層を形成した。

【００３３】次いで、大理石表面（摩面側）に、ポリテトラフルオロエチレン（ＰＴＦＥ）系防汚剤（固形分２０％、水／イソプロピルアルコール＝８０％／２０％分散液）１００部、水／ターペンオイル＝７０部／３０部からなるW／O型エマルジョン液１００部からなる混合液、２００g／m² 相当量を塗布、乾燥後、１００℃下で３０秒間熱処理し、石材表面にフッ素系防汚層を形成した。

【００３４】実施例２

厚さ６mmの大理石の裏面に、ポリエステル長繊維（１０００d－１９２f、原糸強度８g／デニール）よりなる粗目織物（織密度縦横とも２０本／インチ）を重ね合

わせ、エポキシアクリレート系耐食性樹脂（ネオホール８２５０L：日本ユピカ社製）１００部、８％ナフテン酸コバルト０．１部、５５％メチルエチルケトンパーオキサイド（パーメックN：日本油脂製社）１．０部、１００％ジメチルアニリン（試薬）０．０１部からなる混合液を４５０ｇ／m² 相当量塗布後、２５℃下３日間、硬化させ、裏面表面に微細な凹凸を有する裏打ち補強層を形成させた。

【００３５】次いで、大理石表面（摩面側）に、パーフルオロアルキル基含有アクリル系撥水撥油剤（LS３２０：明成化学工業社製）１００部、水／ターペンオイル＝７０部／３０部からなるW／O型エマルジョン液１００部からなる混合液を３００ｇ／m² 相当量塗布、乾燥後、１００℃下で３０秒間熱処理し、石材表面にフッ素系防汚層を形成させた。

【００３６】実施例３

厚さ６mmの白御影石の裏面に、ポリエステル長繊維（１０００ｄ－１９２ｆ、原糸強度８ｇ／デニール）よりなる粗目織物（織密度縦横とも２０本／インチ）を重ね合わせ、エポキシアクリレート系耐食性樹脂（ネオポール８２５０L：日本ユピカ社製）１００部、８％ナフテン酸コバルト０．１部、５５％メチルエチルケトンパーオキサイド（パーメックN：日本油脂社製）１．０部、１００％ジメチルアニリン（試薬）０．１部からなる混合液を５５０ｇ／m² 相当量塗布後、硬化前の耐食性樹脂表面層にケイ砂５号を５００ｇ／m² 相当量付与後、２５℃下３日間、硬化させ裏面表面に、微細な凹凸を有する裏打ち補強層を形成させた。

【００３７】次いで、白御影石表面（摩面側）に、実施例１と同様のPTFE系防汚剤を、３００ｇ／m² 相当量塗布、乾燥後、綿布でブラッシング後、１００℃下で３０秒間熱処理し、石材表面にフッ素系防汚層を形成した。

【００３８】比較例１

石材表面にフッ素系防汚層を形成しない以外は、実施例１と同様の方法で裏打ち補強された大理石を得た。

【００３９】比較例２

粗目織物および耐食性樹脂で裏打ち補強しない以外は、実施例１と同様の方法で、石材表面のみ防汚性を有する大理石を得た。

【００４０】比較例３

補強用の粗目織物を使用しない以外は、実施例１と同様の方法で、石材表面にフッ素系防汚層を形成させ、一方、石材裏面には表面が平坦な耐食性樹脂のみ有する大理石を得た。

【００４１】以上の実施例および比較例にて得られた各種極薄天然石材について、曲げ強度耐衝撃性、接着性、防汚性、撥水性、撥油性、フィールド防汚性、施工性を評価した結果を表２にまとめた。

【００４２】

【表２】

評価項目		実施例1	実施例2	実施例3	比較例1	比較例2	比較例3
5mm厚石材重量：Kg/m2 粗目織物重量：g/m2 耐食性樹脂量：g／m2 耐食性樹脂層表面状態		7．4 150 450 凹凸有	7．4 150 450 凹凸有	7．6 150 550 凹凸大	7．4 150 450 凹凸有	7．4 0 0 平 坦	7．4 0 450 平 坦
1．曲げ破壊荷重：Kg/5cm		12.5	12.6	12.1	12.4	5.8	7.2
2．耐衝撃性		○	○	○	○	×	△
3．接着性：Kg/cm2		10.5	10.6	18.0	10.5	11.0	6.4
4．防汚性	石材表面	○	○	○	×	△	○
	石材裏面	○	○	○	○	×	○
5．撥水性：級	石材表面	3	4	3	1以下	3	3
6．撥油性：級	石材表面	2	3	2	1以下	2	2
7．フィールド防汚性		○	○	○	×	×	○
8．施工性		○	○	○	○	○	○

【発明の効果】本発明の防汚性天然石材は、極薄天然石材の表面にフッ素系防汚剤、裏面に粗目補強布帛および耐食性樹脂を付与し、かつ凹凸性を付形することで、石材表面に、撥水撥油性に基づく優れた防汚性を付与する一方、石材裏面に、良好な裏打ち補強効果と下地との接着性が得られるため、各種汚水および油類等に対して優れた防汚性を示すと共に、雨水、光等の長期間の暴露による、石材表面の光沢、色相および質感の経時変化を効果的に防止することができる。又、曲げ強度と耐衝撃性に対しても優れた改善効果を示す。したがって、従来にない、軽量、かつ強靭で、防汚性に優れた天然石材を提供できるため、施工性が大幅に向上すると同時に、新建材、インテリア用資材として、例えば、床材、壁材、天井材、外壁材、間仕切り材や家具等への利用が可能となり、その効果は、極めて大である。

【図面の簡単な説明】

【図1】

【図2】図1は本発明の防汚性天然石材の1例の断面図を示す図であり、図2は図1の石材の裏面の概略図である。

【図3】

【図4】図3は比較例1の石材の断面を示す図、図4は比較例1の石材の裏面の概略図である。

【図5】

【図6】図5は比較例2の石材の断面を示す図、図6は比較例2の石材の裏面の概略図である。

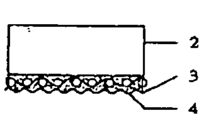
【図7】

【図8】図7は比較例3の石材の断面を示す図、図8は比較例3の裏面の概略図である。

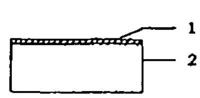
【付号の説明】

1．　フッ素系防汚剤
2．　極薄天然石材
3．　裏打ち補強用粗目織物
4．　裏打ち補強用耐食性樹脂

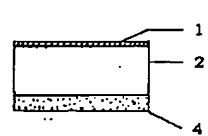
【図3】



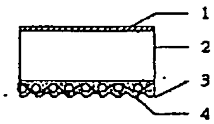
【図5】



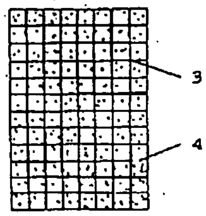
【図7】



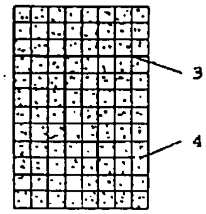
【図1】



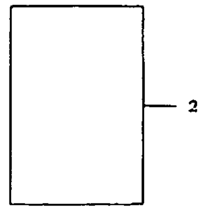
【図2】



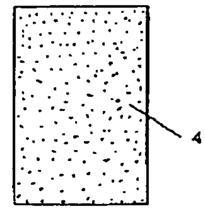
【図4】



【図6】



【図8】



PTO 03-0795

CY=JP DATE=19920820 KIND=A
PN=04-231545

STAINPROOF NATURAL STONE MATERIAL
[Boosei ten'nen sekizai]

Seiichi Ochi, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. December 2002

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(10):	JP
DOCUMENT NUMBER	(11):	04231545
DOCUMENT KIND	(12):	A
PUBLICATION DATE	(43):	19920820
PUBLICATION DATE	(45):	
APPLICATION NUMBER	(21):	02416324
APPLICATION DATE	(22):	19901228
ADDITION TO	(61):	
INTERNATIONAL CLASSIFICATION	(51):	E04F 13/14; B32B 9/00
DOMESTIC CLASSIFICATION	(52):	
PRIORITY COUNTRY	(33):	
PRIORITY NUMBER	(31):	
PRIORITY DATE	(32):	
INVENTOR	(72):	OCHI, SEIICHI; AKEYAMA, ISAMU.
APPLICANT	(71):	TOYOBO CO., LTD.
TITLE	(54):	STAINPROOF NATURAL STONE MATERIAL
FOREIGN TITLE	[54A]:	Boosei ten'nen sekizai

(54) [Title of the Invention] Stainproof Natural Stone Material /273[*]

[Claim(s)] /274

[Claim 1]

A stainproof natural stone material characterized by having a fluorine-based stainproofing agent on the surface of an ultrathin natural stone material and a coarsely-woven cloth and a corrosion-resistant resin layer on its backside.

[Detailed Specifications]

[0001] [Field of Industrial Utilization]

The present invention relates to an ultrathin natural stone material, and in further detail, a lightweight, tenacious stainproof natural stone material with outstanding construction workability and the gloss, color hue and texture surface of the natural stone material does not deteriorate after construction.

[0002] [Prior Art]

Ultrathin natural stone materials have been known in the past using thin slicing techniques utilizing diamond cutters, but although these natural stone materials exhibited outstanding properties from the standpoint of being more lightweight, they had, in addition to their problems including low bending strength and impact resistance, transportability and construction workability from being ultrathin,

[*]Number in the margin indicates pagination in the foreign text.

natural stone materials had other problems such as being stained due to permeation of all sorts of polluted water and oils into the surface and backside, adhesion of dust, and furthermore, the long-term weatherability against rainwater and sunlight.

[0003]

In order to improve such drawbacks, methods in which the backside of natural stone material is reinforced with fabric made from fibers and a resin (publications of Tokko Nos. 51-38731 and 51-48972) have been proposed as methods in which the bending strength and impact resistance were improved. However, in these methods, although the permeation of polluted water into the backside of the stone material can be improved, but the long-term weatherability against various stains on the surface of the stone material, such as stains caused by permeation and adhesion of polluted water and oil, and against rainwater, natural sunlight and artificial sunlight cannot be improved that much, and the long-term and stable use of ultrathin natural stone materials are not adequate.

[0004] [Problems Which the Invention Intends to Solve]

The present invention revives the lightweight features of ultrathin natural stone materials, and moreover, improves some of the drawbacks thereof, i.e., the bending strength and impact resistance over a wide scale, and simultaneously effectively prevents stains on the surface and backside of stone materials caused by permeation of

all sorts of polluted water and oils easily produced especially when the stone material is ultrathin, adhesion of dust, and changes over time in the gloss, color hue and texture of the stone material surface due to long-term exposure to rainwater, the sun, etc. In particular, the more ultrathin a natural stone is, the more apt its strength will decrease and stains caused by permeation of polluted water and the like will become conspicuous especially on relatively soft and porous marble and granite, such as white granite. By solving all the drawbacks of these ultrathin natural stone materials, implementing the design and execution of large-sized natural stone materials which was difficult to realize in conventional methods, and by applying stone materials with outstanding stainproofing properties, the texture and high-grade feeling of the natural stone material itself can be effectively and permanently maintained.

[0005] [Means Used to Solve the Problems]

As a result of painstakingly researching ultrathin natural stone materials, and in particular, relatively soft and porous marbles and granites, such as white granite, and a method for simultaneously solving their drawbacks, i.e., a reduction in the bending strength, impact resistance and facade quality, the inventors of the present invention arrived at the present invention. Namely, the present invention is a stainproof natural stone material characterized by having a fluorine-based stainproofing agent on the surface and a

coarsely-woven reinforcing cloth and a corrosion-resistant resin layer on the backside.

[0006]

In further detail, by uniformly applying a special fluorine-based stainproofing agent having outstanding weatherability (light resistance) and heat resistance, and stainproofing properties in terms of water and oil repellency to the surface of an ultrathin-film natural stone material whose thickness corresponds to 2 to 12 mm, on the one hand, and lining and reinforcing the backside of the stone material with a coarsely-woven reinforcing fabric, a stainproof natural stone material is obtained wherein the drawbacks of ultrathin natural stone materials, i.e., changes over time in the quality of the appearance of the stone material surface after machining can be prevented, and simultaneously, the bending strength and impact resistance over a wide scale are enhanced.

[0007]

The ultrathin stone material of the present invention is one that can be sliced thinly to a thickness of 2 to 12 mm. An extensive range of natural stones including marble and granites, such as white granite, red granite and black granite, are cited for the raw stone that is to be applied, but in particular, marble, white granite, and the like which are relatively soft and porous, are effective as stone materials having color tones that allow stains to stand out with ease.

In contrast to hard, compact stone materials having deep color tones are used for a long period of time, changes over time in the gloss and texture can be prevented, and basically by nature, seldom are changes caused by all sorts of polluted water and the like.

[0008]

Polytetrafluoroethylene and perfluoroalkyl group-containing acryl-based water- and oil-repellents and their denatured materials, such as silicone-denatured fluorine-based compounds, alkylene oxide-denatured fluorine-based compounds, and the like can be cited for the fluorine-based stainproofing agent of the present invention, but it is not particularly limited to these compounds as long as it exhibits outstanding weatherability (light resistance) and heat resistance, as well as its stainproofing properties, i.e., water- and oil-repellency. Polytetrafluoroethylene emulsified dispersions, high fluorine-containing-type (the fluorine content in the solid content is 35% or higher) acryl-based water- and oil-repellents, and silicone-denatured fluorine-based water and oil repellents are particularly preferable for the stainproofing agents having such features.

[0009]

Knit fabrics and non-woven fabrics composed of any of glass fibers, carbon fibers, polyester-based fibers, high-strength, highly-elastic polyethylene-based fibers and aromatic polyamide-based fibers are cited for the coarsely-woven reinforcing fabric, but coarsely-

woven materials are particularly preferable from the standpoint of the reinforcing effect on ultrathin natural stone materials, which is one purpose, and the ease of compounding stone materials and reinforcing fabrics with corrosion-resistant resins. Such textiles generally are preferable as long as they are high in strength and low in elasticity. In order to realize that, the combined use of glass and carbon fibers, and the like, as well as polyester-based fibers and high-strength, highly-elastic polyethylene-based fibers, and the like also is effective. Furthermore, these coarsely-woven reinforcing fabrics can be used after being pretreated for a hard-finish with an alkali-resistant resin, such as a methylolmelamine-, acryl-, unsaturated polyester-, epoxy-, and vinylethylene acetate-based resin.

[0010]

The corrosion-resistant resin in the present invention includes resins with outstanding chemical resistance to a variety of chemicals, such as acids, alkalis, oxidants, reducing agents, various salts, organic solvents, etc.

[0011] /275

Usually, saturated polyester-based resins and unsaturated polyester-based resins, such as HET acid polyester, bisphenol A polyester, and straight-chain vinyl polyester resins, epoxide-based resins, such as glycidyl ether-, glycidyl ester-, glycidyl amine-, linear aliphatic epoxide-, and alicyclic epoxide-based resins, or the

like can be used for such a corrosion-resistant resin, but epoxy acrylate- and bisphenol A polyester-based resins are preferable from the standpoint of adhesiveness to foundations, such as stone, reinforcing fabrics and mortar.

[0012]

In particular, an epoxy acrylate-based resin having outstanding corrosion resistance is used, and in order to give satisfactory reinforcing and stainproofing effects to the backside of the ultrathin natural stone material, a vinyl-based monomer, such as a styrene monomer, can be added to such a resin. The necessary amount of curing agent or curing accelerator may be added after adjusting the viscosity to 500 centipoise or less, and preferably, 100 to 300 centipoise at 20°C, and after uniformly and sufficiently allowing it to permeate the backside and surface of the stone material and into the gaps between the fibers of the reinforcing fabric, it can then be cured at 20 to 140°C for several minutes to about one week.

[0013]

Methyl ethyl ketone peroxide (MEKPO), benzoyl peroxide (BPO), cobalt naphthenate, cobalt octenoate and dimethylaniline are cited for the curing agent or curing accelerator. Usually, an MEKPO/cobalt naphthenate- and BPO/dimethylaniline-based one is used, but use of an MEKPO/cobalt naphthenate/dimethylaniline-based one is particularly effective.

[0014]

The method for applying the fluorine-based stainproofing agent and corrosion-resistant resin in the present invention is explained next. First of all, the fluorine-based stainproofing agent is applied only to the surface portion of the ultrathin stone material. Specifically, after the natural stone material is sliced to the desired thickness, its surface is polished and dried, and then, first, the backside of the stone material is lined and reinforced with a coarsely-woven reinforcing fabric and a corrosion-resistant resin, after which the fluorine-based stainproofing agent is applied to the surface portion of the stone material, and a stainproof layer in terms of the water and oil repellency is formed.

[0015]

In a specific method for applying such a stainproofing agent, a prescribed fluorine-based stainproofing agent is diluted with 0.1 to 20% by weight, and preferably, 2 to 10% by weight of water or an aqueous organic solvent solution, after which an amount corresponding to 20 to 300 g/m^2, and preferably, 50 to 200 g/m^2 is coated evenly on the surface of the stone material and dried, subsequently cured for several minutes to several hours at room temperature to 140°C or less, and preferably, at 40 to 100°C to turn the solution into a film. It is desirable that such a stainproofing agent be applied evenly on the uppermost surface layer portion of the stone material surface, without

uneven permeation, from the standpoint of ensuring the surface quality.

[0016]

Generally, it is difficult to evenly apply the stainproofing agent on the uppermost surface layer portion of the surface of a natural stone material having little homogeneity because the permeability of the stainproofing agent liquid changes subtly, depending on the type and thickness thereof as well as the extent to which it is dried. In order to solve such problems, besides the type, concentration and amount of the stainproofing agent that is to be applied, controlling the extent to which the stone material is dried and the viscosity of the stainproofing agent liquid are extremely important. Controlling the extent to which the stone material is dried depends on the curing conditions for the corrosion-resistant resin at the time the backside of the stone material is reinforced, but ordinarily, after curing is finished, the stone material is cured for 24 hours or longer at room temperature, and subsequently, a stainproof finish is applied. Also, controlling the viscosity of the stainproofing agent liquid somewhat depends on the type and concentration of the stainproofing agent being use, but in order to prevent excess or uneven permeation into the surface of the stone material, it is desirable that it be used in a range of 100 to 3,000 centipoise, and preferably, 200 to 1,000 centipoise. If the viscosity

of the stainproofing agent liquid is less than 100 centipoise, uneven permeation occurs. By contrast, if it is higher than 3,000 centipoise, uneven adhesion of the stainproofing agent to the surface easily arises.

[0017]

The method in the present invention for applying the corrosion-resistant resin to the backside of the stone material will now be explained. For such an application method, there is ① a method in which the coarsely-woven reinforcing fabric is laminated on the backside of the ultrathin natural stone material, after which it is coated or injected with the corrosion-resistant resin, ② a method in which the backside of the ultrathin natural stone material is coated with the corrosion-resistant resin, subsequently laminated with the coarsely-woven reinforcing fabric, and then further coated or injected with the corrosion-resistant resin, ③ a method in which the coarsely-woven reinforcing fabric is impregnated with the corrosion-resistant resin and cured in advance to make a sheet-shaped prepreg, after which the backside of the ultrathin stone material is coated with the corrosion-resistant resin, and the prepreg is laminated on and adhered to it. The amount of the corrosion-resistant resin to be applied varies, depending on the type and thickness of the natural stone material, the type of the reinforcing fabric and the applications for the stone material, but ordinarily, it is selected and used in a range

of 100 to 1,500 g/m^2, and preferably, 200 to 500 g/m^2. The corrosion-resistant resin curing conditions of 20 to 140°C, and in particular, 20 to 60°C are preferable from the standpoint of preventing the lined, reinforced stone material from being warped and deformed, and maintaining the physical properties of the stone material and the surface quality, such as the gloss and color hue. Moreover, the lined and reinforced backside of the natural stone material has moderate surface roughness, so the as long as it is dry enough, it exhibits satisfactory adhesiveness.

[0019]

One method for improving the adhesiveness between the lined, reinforced surface and a mortar cement or a dry adhesive is one in which unevenness is formed on the lined, reinforced surface using the corrosion-resistant resin. Such a method includes ① one in which the amount of the corrosion-resistant resin applied is controlled by utilizing the variation in the height of the coarsely-woven reinforcing fabric, ② one in which an amount corresponding to 100 to 1,500 g/m^2 of inorganic particles, such as silica sand, having satisfactory adhesiveness to foundations, such as mortar, is applied to the surface of the corrosion-resistant resin, and subsequently cured, ③ one in which a separately-formed, unevenly-shaped sheet or plate is press-fitted to the surface of the corrosion-resistant resin which is then cured, and subsequently peeled off to shape it, among

other methods.

[0020]

The "surface of the natural stone material" in the present invention ordinarily means the 'polished' side and the "backside" means the rough side.

[0021] [Practical Examples]

The present invention will be explained specifically below by citing practical examples. "%" in the practical examples wholly denotes "% by weight."

[0023]

The properties of the stainproof natural stone material were measured in the following methods.

[0024] 1. Bending strength (bending breaking load)

This was measured by cutting each stone material to a size of 5 cm wide × 20 cm long according to the method in JIS A 1408 (sample size: 5 cm×20 cm; bending speed: 1 mm/min.;
curvature radius of bending bar: 5 mm; distance between /276
supporting points: 15 cm).

[0024] 2. Impact resistance

According to the method in JIS A 1421 (sample size: 20 cm×20 cm; sample support: support of entire sample surface on sand; weight (W1): 1,000 g; falling height: 100 cm), a stone material surface without any change after the impact test was taken as "O," a surface with cracks

was taken as "Δ," and a surface where the stone material was destroyed was taken as "×."

[0025] 3. Adhesive

A compounded mortar ("Adokeep [transliteration]," made by Tokuyama Soda) with a thickness corresponding to 50 mm was adhered to the backside of a 10 cm^2 piece of stone material, cured for 3 weeks at room temperature, and the bond strength was measured by using a Kenken-type tensile tester.

[0026] 4. Stainproofing properties

An amount corresponding to 10 cc of polluted water containing 22 cc/L of blue ink, 5 cc/L of heavy B-grade oil and 100g/L of clay was dripped on the surface and backside of a 10 cm^2 stone material, covered with a film, subsequently set aside for one week at room temperature, and then wiped off with a damp towel. The extent of stains on the surface and backside of the stone material after drying wherein there were no stains at all was taken as "○," where stains were present was taken as "Δ," and where stains were conspicuous was taken as "×."

[0027] 5. Water repellency

Droplets of an isopropyl alcohol/water mixture were dripped on the surface of a 10 cm^2 stone material, and the level of the damp state was judged from 1 (poor) to 5 (good).

[0028] [Table 1]

Aqueous Isopropyl Alcohol Solution Composition

Water repellency level	Composition (VOL%)	
	Isopropyl alcohol (high-grade reagent)	Water
5	60	40
4	32	68
3	21	79
2	15	85
1	9	91

[0029] 6. Oil repellency

The oil repellency on the stone material surface was measured according to the evaluation for oil repellency in AATCC-118-1975 and the level was judged from 1 (poor) to 8 (good).

[0030] 7. Stainproofing properties in field

The backside of a 50 cm^2 was adhered horizontally to a mortar cement foundation, a 2-year exposure test was performed outdoors, and the change in the appearance (gloss, color hue) of the stone material surface was judged visually. A backside without any change at all was judged as "◎," one with a subtle change was judged as "○," one with a

slight change was judged as "Δ," and one with a major change was judged as "×."

[0031] 8. Construction workability

The ease and difficulty of a lateral shifting workability and adhesion workability were shown together when a 1 m wide × 1.5 m long piece of stone was used in construction work involving adhesion with mortar. A workability that was easier than for a stone material having the usual thickness of 12 mm or more was taken as "O" and one that was more difficult was taken as "×."

[0032] Practical Example 1

The backside of a 6 mm thick piece of marble was overlapped with a coarsely-woven fabric (warp/woof fiber density: 20 fibers/in.) comprising long polyester fibers (1000d-192f, thread strength: 8 g/denier), an amount corresponding to 450 g/m^2 of a liquid mixture comprising 100 parts of epoxy acrylate-based corrosion-resistant resin (Neopole 8250L, made by Japan U-PICA Co., Ltd.), 0.1 part of 8% cobalt naphthenate, and 1.0 parts of 55% methyl ethyl ketone peroxide (Permeck N, made by NOF Corp.) was coated on it, subsequently cured for 5 days at 25°C, and a reinforcing layer having a subtle unevenness was formed on the backside and surface.

[0033]

An amount corresponding to 200 g/m^2 of a liquid mixture comprising 100 parts of polytetrafluoroethylene (PTFE)-based

stainproofing agent (20% solid content; water/isopropyl alcohol = 80%/20%/20% dispersion)and 100 parts of a W/O emulsion comprising 70 part/30 parts of water/terpene oil was coated on the surface (polishing side) of a piece of marble, dried, and subsequently heat-treated for 30 seconds at 100°C to form a fluorine-based stainproof layer on the surface of stone material.

[0034] Practical Example 2

The backside of a 6 mm thick piece of marble was overlapped with a coarsely-woven fabric (warp/woof fiber density: 20 fibers/in.) comprising long polyester fibers (1000d-192f, thread strength: 8 g/denier), an amount corresponding to 450 g/m^2 of a liquid mixture /277 comprising 100 parts of epoxy acrylate-based corrosion-resistant resin (Neopole 8250L, made by Japan U-PICA Co., Ltd.), 0.1 part of 8% cobalt naphthenate, 1.0 parts of 55% methyl ethyl ketone peroxide (Permeck N, made by NOF Corp.), and 0.01 part of 100% dimethylaniline (reagent) was coated on it, subsequently cured for 3 days at 25°C, and a lining, reinforcing layer having a subtle unevenness was formed on the backside and surface.

[0035]

An amount corresponding to 300 g/m^2 of a liquid mixture comprising 100 parts of a perfluoroalkyl group-containing acryl-based water and oil repellent (LS320, made by Meisei Kagaku Kogyo K.K.) and 100 parts of a W/O emulsion comprising 70 part/30 parts of

water/terpene oil was coated on the surface (polishing side) of a piece of marble, dried, and subsequently heat-treated for 30 seconds at 100°C to form a fluorine-based stainproof layer on the surface of stone material.

[0036] Practical Example 3

The backside of a 6 mm thick piece of white granite was overlapped with a coarsely-woven fabric (warp/woof fiber density: 20 fibers/in.) comprising long polyester fibers (1000d-192f, thread strength: 8 g/denier), an amount corresponding to 550 g/m^2 of a liquid mixture comprising 100 parts of epoxy acrylate-based corrosion-resistant resin (Neopole 8250L, made by Japan U-PICA Co., Ltd.), 0.1 part of 8% cobalt naphthenate, 1.0 parts of 55% methyl ethyl ketone peroxide (Permeck N, made by NOF Corp.), and 0.1 parts of a 100% dimethylaniline reagent was coated on it, subsequently an amount corresponding to 500 g/m^2 of No. 5 silica sand was applied to the uncured corrosion-resistant resin surface layer and then cured for 3 days at 25°C, and a lining and reinforcing layer having a subtle unevenness was formed on the backside and surface.

[0037]

Next, the surface (polished side) of a piece of white granite was coated with an amount corresponding to 300 g/m^2 of the same PTFE-based stainproofing agent as in Practical Example 1, subsequently brushed with a cotton cloth, and then heat-treated for 30 seconds at 10°C to

form a fluorine-based stainproof layer on the stone material surface.

[0038] Comparative Example 1

Except for the fact that a fluorine-based stainproof layer was not formed on the stone material surface, a lined, reinforced piece of marble was obtained in the same method as in Practical Example 1.

[0039] Comparative Example 2

Except for the fact that not there was no lining or reinforcing with a coarsely-woven fabric and a corrosion-resistant resin, a piece of marble having stainproofing properties on the stone material surface only was obtained in the same method as in Practical Example 1.

[0040] Comparative Example 3

Except for the fact that a coarsely-woven fabric for reinforcement use was not used, a fluorine-based stainproof layer was formed on the stone material surface in the same method as in Practical Example 1, on the one hand, and only a piece of marble having a flat-surface corrosion-resistant resin on the stone material backside was obtained.

[0041]

The results upon evaluating the bending strength, impact resistance, adhesiveness, stainproofing properties, water and oil repellency, stainproofing properties in the field, and construction workability for the various ultrathin natural stone materials obtained

in the above practical examples and comparative examples were shown together in Table 2.

[0042] [Table 2]

/278

Evaluated Item		Practical Example 1	Practical Example 2	Practical Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
5 mm thick rock material weight: Kg/m2		7.4	7.4	7.6	7.4	7.4	7.4
Coarsely woven material weight: g/m2		150	150	150	150	0	0
Corrosion-resistant resin amount: g/m2		450	450	550	450	0	450
Corrosion-resistant resin layer surface state		Uneven	Uneven	Highy uneven	Uneven	Flat	Flat
1. Bending breaking load: Kg/5 cm		12.5	12.8	12.1	12.4	5.8	7.2
2. Impact resistance		○	○	○	○	×	△
3. Adhesiveness: Kg/cm2		10.5	10.6	18.0	10.5	11.0	6.4
4. Pollution resistance	Rock material surface	○	○	○	×	△	○
	Rock material surface	○	○	○	○	×	○
5. Water repellency: level	Rock material surface	3	4	3	At most 1	3	3
6. Oil repellency: level	Rock material surface	2	3	2	At most 1	2	2
7. Stainproofing properties in field		○	○	○	×	×	○
8. Workability		○	○	○	○	○	○

[Advantages of the Invention]

The stainproof natural stone material of the present invention exhibits outstanding stainproofing properties against all sorts of polluted water, oils and the like because outstanding stainproofing properties, i.e., water and oil repellency is given to the stone material surface by applying the fluorine-based stainproofing agent on the surface of the ultrathin natural stone material and applying a coarsely-woven reinforcing fabric and corrosion-resistant resin on the backside, on the one hand, and also because a satisfactory lining and reinforcing effect and adhesiveness to foundations are obtained, and at the same time, the gloss, color hue and texture of the stone material surface can be effectively prevented from changing over time due to long-term exposure to rainwater, sun, etc. Also, it exhibits outstanding effects for improving the bending strength and impact resistance. Therefore, a lightweight, tenacious natural stone material with outstanding stainproofing properties also can be obtained, unlike in the past; hence, the construction workability is improved over a wide scale. At the same time, it can be utilized as a new construction material and material for indoors, such as for flooring, wall materials, ceiling materials, outdoor facade materials, partitioning materials, and furniture; hence, its advantages are extremely large.

[Brief Description of the Figures]

(Figure 1 is a drawing showing a cross section of one (1) example of the stainproof natural stone material of the present invention.)

[Figure 1]

[Figure 2] Figure 1 is a drawing showing a cross section of one (1) example of the stainproof natural stone material of the present invention. Figure 2 is a schematic view of the backside of the stone material in Fig. 1.

[Figure 3]

[Figure 4] Figure 3 is a drawing showing a cross section of the stone material of Comparative Example 1. Figure 4 is a schematic view of the backside of the stone material of Comparative Example 1.

[Figure 5]

[Figure 6] Figure 5 is a drawing showing a cross section of the stone material of Comparative Example 2. Figure 6 is a schematic view of the backside of the stone material of Comparative Example 2.

[Figure 7]

[Figure 8] Figure 7 is a drawing showing a cross section of the stone material of Comparative Example 3. Figure 8 is a schematic view of the backside in Comparative Example 3.

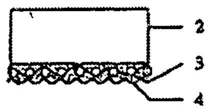
[Explanation of the Codes]

1. fluorine-based stainproofing agent
2. ultrathin natural stone material

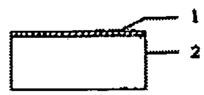
3. coarsely woven fabric for lining and reinforcement

4. corrosion-resistant resin for lining and reinforcement

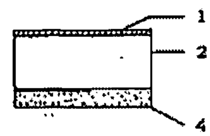
[Figure 3]



[Figure 5]

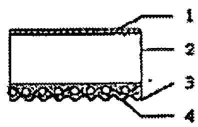


[Figure 7]

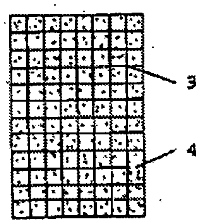


/279

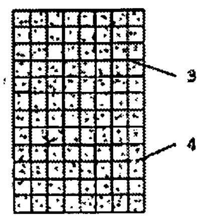
[Figure 1]



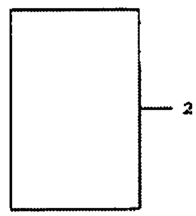
[Figure 2]



[Figure 4]



[Figure 6]



[Figure 8]